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Submillimeter EPR spectroscopy of Van Vleck paramagnets holmium nicotinate dihydrate and KY_3F_{10}:Ho

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Abstract

Results of EPR measurements of the Van Vleck paramagnets (monoclinic holmium nicotinate dihydrate and activated cubic complex fluoride KY_3F_{10}:Ho^{3+}) are presented. Spectra were taken with a wide-band spectrometer operating in the frequency range 65–535 GHz at liquid helium temperature for magnetic fields up to 1 T. Transformations of the hyperfine structure of the EPR spectra with the frequency of the radiation and the directions of the constant and alternating magnetic fields have been studied and compared with results of calculations based on a diagonalization of the complete electronic–nuclear Hamiltonian. Crystal field splittings between the ground and first excited singlets of 7.3 cm^{-1} in holmium nicotinate and 5.8 cm^{-1} in KY_3F_{10}:Ho have been estimated using extrapolations of the resonance frequency dependences on magnetic field to zero field strength.

Keywords: Crystal field; Hyperfine interaction; Paramagnetic resonance

1. Introduction

Electron paramagnetic resonance (EPR) is a very informative physical method of studying crystal fields in paramagnets. However, conventional EPR spectrometers cannot be used effectively to study the Van Vleck paramagnets containing non-Kramers lanthanide ions. If a non-Kramers ion is located in a low symmetry crystal field, each of its manifold should be split into $2J+1$ singlets. Methods of EPR spectroscopy in the submillimeter range of wavelengths make it possible to investigate magnetic and electric dipole transitions between singlet Stark sublevels. All data on submillimeter EPR spectra known to date correspond to transitions between the Zeeman sublevels of the ground state Kramers [1–3] or non-Kramers [3–8] doublets or quasi-doublets with small zero field splitting [3,9] and to transitions between the ground singlet and excited doublet [10], the ground doublet and excited singlet [3,8], doublet [1,3] or triplet [5] Stark sublevels of the ground multiplet of magnetically equivalent lanthanide ions. Measurements were usually performed with the alternating magnetic field $\boldsymbol{H}_1(t)$ perpendicular to the static magnetic field $\boldsymbol{H}$. In the present study, EPR spectra of Ho^{3+} ions in the Van Vleck paramagnets KY_3F_{10}:Ho (KYF:Ho) and holmium nicotinate dihydrate (HoND), with resolved hyperfine structure of magnetic dipole singlet–singlet transitions, are obtained in weak magnetic fields (under the condition $g_J\mu_B H \ll \Delta$, where g_J is the Lande factor of the ground $^5I_8$ multiplet, μ_B is the Bohr magneton and Δ is the zero field splitting). In contrast to compounds with a magnetic ground state, we do not need to use strong magnetic fields to suppress the magnetic broadening of the spectral lines in Van Vleck paramagnets. Line intensities in EPR spectra depend on the effectiveness of the modulation of the singlet–singlet splitting with magnetic field, and the optimal conditions for observing intense EPR

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